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Dissolved uranium, radium and radon evolution in the Continental Intercalaire aquifer, Algeria and Tunisia

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ABSTRACT

Natural, dissolved ^{238}U-series radionuclides (U, ^{226}Ra, ^{222}Rn) and activity ratios (A.R.s: ^{234}U/^{238}U; ^{228}Ra/^{226}Ra) in Continental Intercalaire (CI) groundwaters and limited samples from the overlying Complexe Terminal (CT) aquifers of Algeria and Tunisia are discussed alongside core measurements for U/Th (and K) in the contexts of radiological water quality, geochemical controls in the aquifer, and water residence times. A redox barrier is characterised downgradient in the Algerian CI for which a trend of increasing ^{234}U/^{238}U A.R.s with decreasing U-contents due to recoil-dominated ^{234}U solution under reducing conditions allows residence time modelling ~500 ka for the highest enhanced A.R. = 3.17. Geochemical modelling therefore identifies waters towards the centre of the Grand Erg Oriental basin as palaeowaters in line with reported ^{14}C and ^{36}Cl ages. A similar ^{234}U/^{238}U trend is evidenced in a few of the Tunisian CI waters. The paleoage status of these waters is affirmed by both noble gas recharge temperatures and simple modelling of dissolved, radiogenic ^{4}He-contents both for sampled Algerian and Tunisian CI and CT waters. For the regions studied these waters therefore should be regarded as "*fossil*" waters and treated effectively as a non-renewable resource.

1. Introduction

Low-level activity, naturally-occurring uranium- and thorium-series radionuclides and their isotopes in groundwaters can give insight into reduction–oxidation (redox) and geochemical controls, water–rock interactions, aquifer mixing, and subsurface residence times of sampled waters in aquifer systems (Andrews, 1991; Bonotto, 2004; Porcelli, 2008). They also have significance for health in terms of their alpha (α-)radioactivity, and many countries have adopted regulatory standards for water use (cf. Chau et al., 2011).

In semi-arid and arid zones in Algeria, groundwater is the principal source of drinking water; and in Tunisia in 2010 the Ministry of Agriculture developed a strategic survey for sustainable water usage by 2050 which could include the use of non-traditional sources of water like desalination of seawater or salty groundwater.

In Algeria, Amrani (2002) has measured bottled mineral waters (for 8 samples: 2.6–14 Bq/l ^{222}Rn; 12–37 mBq/l ^{226}Ra; 15–39 mBq/l ^{232}Th; 0.4–1.6 Bq/l ^{40}K). Amrani et al. (2000) have published ^{222}Rn measurements as 0.5–19.37 Bq/l (15 samples, only one sample > 11 Bq/l) in groundwater from springs and deep wells of the Tassili N'Ajer high sandstone plateau in southeast Algeria. Most recently, Aït-Ziane et al. (2012) have reported groundwater ^{222}Rn data (21 samples: 0.1–34.4 Bq/l, mean = 11.5 Bq/l) and ^{226}Ra (11 samples: 0.25–5 Bq/l) for the Chott El Hodna (Algeria) region. Much higher concentrations of ^{222}Rn may be associated with oil and gas production (Hamlat et al., 2003) as radon is also a noble gas which naturally and preferentially partitions to non-aqueous liquid and gas phases. High natural radium concentrations have been reported associated also with palaeowaters, e.g. in the Disi sandstone aquifer in Jordan (Vengosh et al., 2009).

The Continental Intercalaire (CI) formation in North Africa hosts an extensive, regional, internally-drained (endorheic), sedimentary aquifer which underlies Algeria, Tunisia, and Libya. Castany (1981) originally emphasised the deep-basin nature of this aquifer system of the northern Sahara such that "development and management of water stored in aquifer … … [is] 'groundwater mining'". Puri et al. (2006), Mamou et al. (2006) and Edmunds (2012) have asserted

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that in the Saharan basins the water resource often can be shown to be '*fossil*' or palaeowater, almost entirely non-renewable in terms of both their water resources management and in International Law (Eckstein and Eckstein, 2003, 2005). Semi-arid/arid regions like Libya and Algeria are heavily dependent on groundwater as their only water resource; coordinated management of this trans-boundary, shared water resource led to the creation of a Consultation Mechanism Unit for the North Sahara Aquifer System – SASS (Système Aquifere du Sahara Septentrional) in July 1999 (UNESCO, 2010).

Previous attempts to date the geochemical residence times of the Algerian CI waters using ^{14}C ($\tau_{1/2}$ = 5730 a: Gonfiantini et al., 1974; Sonntag et al., 1978; Guendouz, 1985; Elliot, 1990; Guendouz et al., 1997; Edmunds et al., 2003) identified that, apart from aquifer margins, the sampled CI waters all have low radiocarbon activities (<5 per cent modern carbon, pmc). Towards the centre of the basin, waters are very close to the limit of age discrimination by the radiocarbon method (~25–30 ka). This along with past climatic signatures archived in the waters through their stable isotopes of water signatures (δ^2H, $\delta^{18}O$) and dissolved noble gas contents (Elliot, 1990; Guendouz et al., 1997) appear to confirm their palaeowater status. Moreover, Guendouz and Michelot (2006) report ^{36}Cl ($\tau_{1/2} = 3 \times 10^5$ a) dates for CI waters suggesting minimum model groundwater ages of 0–134 ka and maximum ages 49–223 ka for relevant samples on the M'Zab ridge (Berriane, Metlili) and ages > 100 ka (Zelfana, El-Hadjira), although initial $^{36}Cl/Cl$ data are being revised (Petersen et al., 2014a, in press).

Recent literature however has queried the significance and presumption of the paleowater/*fossil* water status (and by implication a stagnant/null recharge or disconnected flow system) particularly for the North-Western Sahara Aquifer System. Al-Gamal (2011) invokes stratification and regional mixing of modern and palaeowaters generally in the system on the basis of moderately-depleted δ^2H, $\delta^{18}O$ signatures seen in recharge zones, and states particularly that tritium (^3H; $\tau_{1/2}$ = 12.32 a) is widespread – although few data are presented and even the presence of ^{14}C signatures > 2 pmc would translate to significant geochemical residence times (Annexe 8, OSS, 2003). From piezometric modelling of the CI aquifer Ould Baba Sy (2005), suggests that a null recharge presumption for the Tademait and Tinrhert plateaux of southern Algeria is reasonable, however he queries null recharge in the Algerian Saharan Atlas and the Dahar Hills (Tunisia) and also the Algerian M'zab (at least for the CT aquifer). Gonçalvès et al. (2013) deploy a regional water balance approach to assess natural recharge, although since all aquifers are distributed flow systems water recharging at any location then is flowing somewhere specific and for water resources management and sustainability of any aquifer equating safe aquifer yield to its natural recharge can be problematic (e.g. Elliot et al., 1998, 2001; Sophocleous, 1997).

Radioactive ^3H, ^{14}C and ^{36}Cl dating methods are all based on a 'decay clock' of atmospheric inputs at recharge (albeit with various correction mechanisms for mixing sources and dilution within an aquifer). Natural ^{238}U ($\tau_{1/2} = 4.5 \times 10^9$ a)- and ^{232}Th ($\tau_{1/2} = 1.405 \times 10^{10}$ a) decay is internal to the system, which can provide an 'accumulation clock' for their products – including other U- and Th-isotopes, Ra, Rn (all radioactive) and also (stable) dissolved ^4He (since the U- and Th-series decay mechanism is predominantly by α-emission). Whilst natural dissolved U distributions and $^{234}U/^{238}U$ activity ratios (A.R.s) in Continental Intercalaire (CI) waters have been reported (Edmunds et al., 2003; Chkir et al., 2009), the radiogenic and radioactive daughters ^{226}Ra and ^{222}Rn have not been reported previously. Moreover, $^{234}U/^{238}U$ disequilibria modelling for these deep basin waters in terms of groundwater dating and as a comparative check for consistency of groundwater ages by other methods in the Algerian aquifer has not been attempted to date. Preliminary results for CI waters in the Tunisian aquifer by Petersen et al. (2013) and Fröhlich (2013) suggest residence times ~500 ka based on an apparent decreasing trend of $^{234}U/^{238}U$ activity ratios (^{234}U $\tau_{1/2} = 244.5 \times 10^3$ a) with increasing U-contents (see also Bonotto, 2006). In the current study, the evolution of U, $^{234}U/^{238}U$ A.R., ^{226}Ra (including $^{228}Ra/^{226}Ra$ A.R.), and ^{222}Rn systematics particularly along a flow line in the Algerian CI are discussed in terms of ^{238}U-series systematics and groundwater dating (including also ^4He ages).

2. Study area

The Continental Intercalaire (CI) aquifer underlies continuously an area ~600,000 km^2 in Algeria and Tunisia (Castany, 1982) and ~100,000 km^2 overall (including Libya). In Algeria, the M'Zab Ridge running N–S (Fig. 1) structurally provides a watershed divide between (to the west) the Grand Erg Occidental and (to the east) the Grand Erg Oriental hydrogeological basins. The shallower, overlying Complexe Terminal (CT) aquifer covers ~35,000 km^2. In the Grand Erg Occidental the two aquifers are hydraulically connected (cf. Moulla et al., 2012), whereas in the Grand Erg Oriental the two aquifers are separated by semi-permeable/impermeable layers and confined, artesian conditions exist for the CI aquifer towards the centre of this basin.

The CI formation comprises permeable continental detrital deposits of sand-sandstone and argillaceous sands with intercalations of marine clays and arenaceous clays of Lower Cretaceous (Albian) age (Furon, 1963). Except at its borders and in the western and Djeffara sub-basins, the CI aquifer is confined over the major part by a series of Upper Cretaceous (predominantly Cenomanian) transgressive clays with evaporites. Underlying the whole of the central region from Hassi Messaoud to the great salt-lake Chotts in the N is the confining basal Upper Jurassic Malm. The CT aquifer groups under the same name several very heterogeneous formations: permeable beds of (Upper Cretaceous) Senonian limestones, with Turonian dolomites on the borders (Dahar, M'Zab), and (Tertiary) Mio-Pliocene sands (the CT proper). Guendouz (1985) includes within this CT unit the phreatic aquifer system of the Quaternary aeolian dunes.

The recharge area for the CI aquifer in the Algerian study area is in the Atlas Mountains ~400 km to the NW (Gonçalvès et al., 2013; Fig. 1). The aquifer is hydraulically continuous from here to the Chotts of Tunisia where it discharges. Groundwater samples for radioelements and their isotopes have been taken (Fig. 1) from 12 wells in the Eastern Great Erg (Grand Erg Oriental) basin of Algeria, samples A1–A10 follow a NW–SE radial flow direction identified originally by Guendouz (1985, his Fig. 3) from piezometric data for the CI aquifer and confirmed from the latest piezometric map (OSS, 2003, Planches 10–13). Two samples (A12, A13) were taken from the overlying, shallower CT aquifer, and a further CI sample from a new well (A14) to the North.

A dozen groundwater samples from Tunisia are also reported here: 7 in the CI proper, 2 in the CT, and 3 associated with both aquifers (CI/CT). Major flow directions in the extensive CI aquifer system (Fig. 1) appear broadly to converge on the major Chotts west of Gabès in Tunisia: W–E from the Saharan Atlas to Chott Djerid and the Gulf of Gabès; SW–NE from the M'zab ridge region of southwestern Algeria and the Tademait Plateau and/or the Tinrhert Plateau (S–N) towards Chott Fedjej/Gulf of Gabès; S–N from local recharge in the Dahar uplands in southern Tunisia. The Tunisian CI samples presented here generally are located to the East of the horst structure identified around the region of Tozeur (T9; cf. Edmunds et al., 2003, their Fig. 13) and likely therefore the flow direction is oriented predominantly S–N from the Tinrhert plateau of southern Algeria or the Tunisian Dahar Hills as the possible

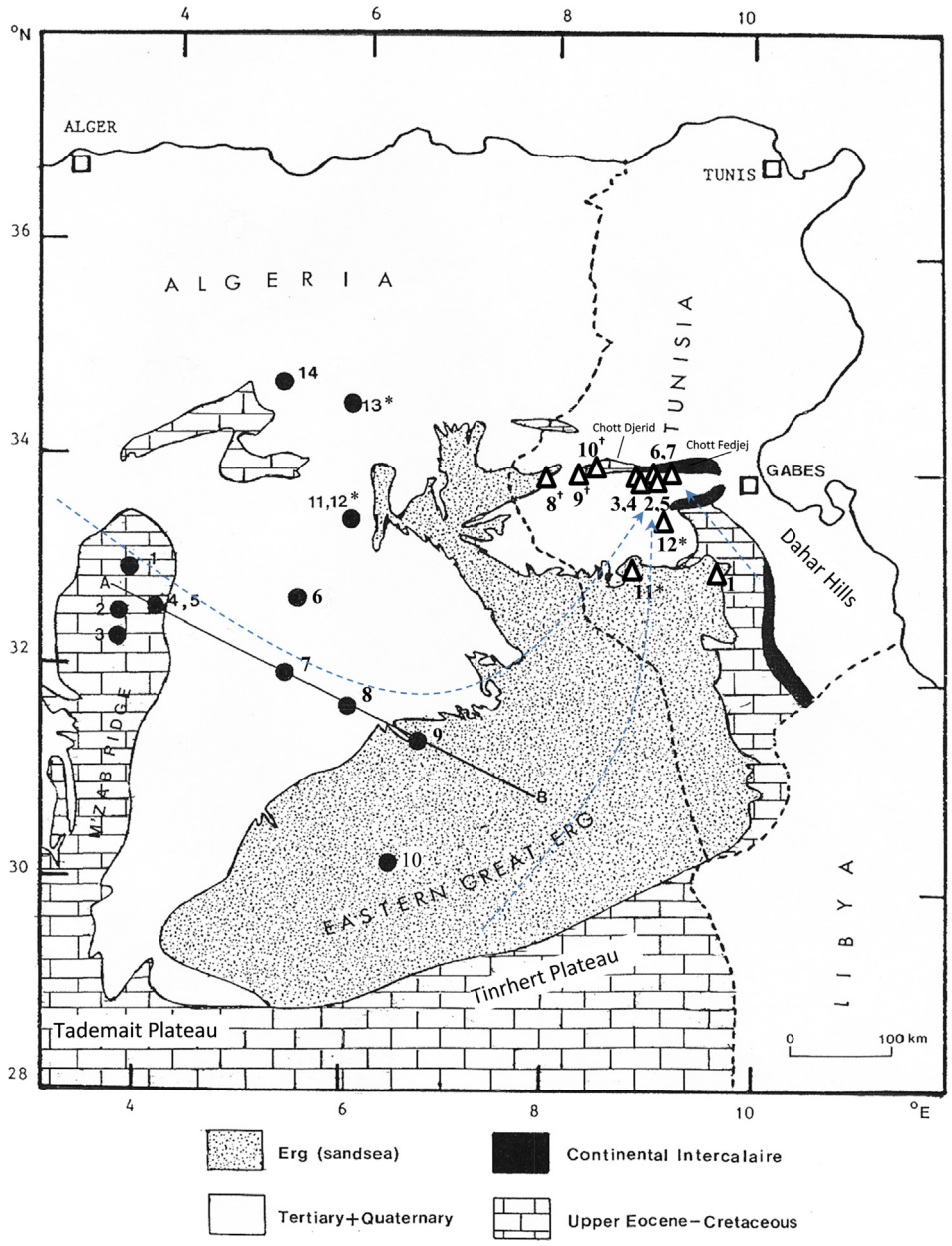

Fig. 1. Schematic diagram showing geological outcrops and groundwater sampling locations in the deep Continental Intercalaire (CI) sandstone aquifer of the Grand Erg Oriental (Algeria) and Tunisia basins. The M'Zab Ridge running N–S structurally provides a watershed divide between (to the west) the Grand Erg Occidental and (to the east) the Grand Erg Oriental hydrogeological basins in Algeria. Samples 1–10 follow a NW–SE radial flow direction (Line AB) identified originally by Guendouz (1985, his Fig. 3) from piezometric data for the CI aquifer. Samples identified with a * were taken from the shallower, overlying Complexe Terminal (CT) aquifer; samples identified † (Tunisia only) are associated with both (CI/CT). Closed circle locations (Algeria); open triangles (Tunisia). Also shown (broken lines) are the general flowlines in the Continental Intercalaire based on piezometric contours given in OSS (2003, their Planche 11).

recharge areas, following the piezometric contours (OSS, 2003). Sample numbering then is S–N for the Tunisian CI samples (T1–T7) proper and also other samples (T8–T10 are CI/CT; T11, T12 are CT).

Two borehole sites in Tunisia were also sampled at depth for aquifer solids (Chott Fedjej F1 in the CI; Negga N6 in the CT) giving possible representative Th/U/K rock data for these aquifers in the study region.

3. Material and methods

Borehole and field sampling details for the Algerian samples are given in Elliot (1990). Water samples for the determination of total dissolved U-content and $^{234}U/^{238}U$ activity ratio were collected in 60 L acid-washed polyethylene containers. On collection, samples were acidified in the field to pH < 2 and a tracer spike of ^{236}U (0.185 ± 0.002 Bq, representing a coverage factor $k = 2$) added to quantify the chemical yield of U extraction, in addition to 900 mg of Fe^{3+} carrier. In the laboratory, U was co-precipitated with Fe^{3+} under alkaline conditions, then separated from Fe, Ca, Mg and other elements in the precipitate by solvent extraction and ion-exchange procedures (Andrews and Kay, 1983). The isotopes of uranium were co-precipitated on $Fe(OH)_3$ by increasing the pH to 7–8 through addition of concentrated NH_4OH solution. The precipitate was recovered, dissolved in 9 mol/dm^3 HCl and Fe^{3+} was extracted into an equal volume of methyl isobutyl ketone. The acid solution of uranium was further purified by anion exchange, first on a Cl^- and

then on a NO_3^- column of Biorad AG1-X8 100–200 mesh resin. U was finally eluted from the NO_3^- column with 0.1 mol/dm^3 HCl, evaporated to dryness, dissolved in 10-cm^3 2 mol/dm^3 $(NH_4)_2SO_4$ solution, and transferred to a teflon electrolysis cell. Electrodeposition of U on a stainless steel planchet was complete after 3 h at a current density of 1 A/cm^2. The α activities were determined with 100 μm depletion depth, 450 mm^2 area Passivated Implanted Planar Silicon (PIPS) detectors, whose typical backgrounds in the ^{238}U, ^{236}U and ^{234}U energy regions were (0.001 ± 0.0002), (0.0009 ± 0.0002) and (0.0028 ± 0.0003) cpm (counts per minute) respectively. The spectra for natural U and ^{236}U tracer extracted were recorded on a Canberra, 2048-channel, multi-channel analyser, where the concentration data were calculated from the counting rates of ^{238}U and ^{236}U peaks and the ^{234}U/^{238}U activity ratio data were calculated from the counting rates of ^{238}U and ^{234}U peaks. Samples for dissolved radiogenic ^{222}Rn determination were collected in gas-tight throughflow bottles with sealable inlet and outlet tubes. Samples were generally analysed within two weeks of collection. The ^{222}Rn was outgassed into a scintillation flask using a N_2 stream and its activity determined by α-scintillation counting. The counting efficiency of each scintillation flask was determined using standard ^{226}Ra solutions that allowed estimation of an average detection limit of 98 mBq/L. Samples for Ra determinations were filtered (0.45 μm) into a 5 L acid-washed container, and acidified. Recovered samples for ^{226}Ra contents were transferred to glass de-emanation bottles and ^{222}Rn outgassed using N_2. The bottles were sealed and left one month for ingrowth of ^{222}Rn to its equilibrium activity with ^{226}Ra, subsequently determined as for dissolved Rn samples. Samples for Ra activity ratios were recovered using the MnO_2 powder scavenging method, subsequently leached with 2 M HNO_3 and co-precipitated as $Ba(Ra)SO_4$. Radium isotope activities were then determined by γ-spectrometry with Ge(Li) detector (cf. Michel et al., 1981).

For α-spectrometric determinations on core samples representative 1 g splits from bulk samples crushed to <10 μm were totally dissolved by acid treatment (HF, $HClO_4$) following the addition of tracer spikes of ^{236}U (0.153 ± 0.003 Bq, representing a coverage factor $k = 2$) and ^{229}Th (0.201 ± 0.004 Bq, representing a coverage factor $k = 2$). Following separation by anion exchange, U and Th were electrodeposited onto stainless steel discs. For γ-spectrometric determinations samples were crushed to <1 mm and 200 g weighed in to a tin, sealed and stored for 20 days to establish secular equilibration with ^{222}Rn, ^{214}Pb, ^{214}Bi. The sample then was counted on a 6″ (diameter) × 4″ NaI (Tl) crystal using a multichannel analyser.

Geochemical speciation modelling including mineral saturation indices (SI) was performed using the original WATEQ4F code (Ball et al., 1987) incorporating the uranium thermodynamic database of Ball et al. (1981).

4. Results and discussion

For the Algerian CI aquifer samples, borehole screened intervals for samples are 200–500 m (M'Zab Ridge: A1–A3) with water sampling temperatures (ST) in the range 30.7–31.5 °C. Away from the M'Zab Ridge sampling depths are 800–1600 m with ST up to 57.7 °C, demonstrating the depth (and geothermal potential) of these waters. For CT aquifer samples, sampling depths are 145 m (A12), but 1000 m at A13 with sampling temperatures 24.4 and 47.1 °C, respectively. Dissolved O_2 (DO) values were 3–8 ppm on and close to the M'Zab Ridge (A1–A5) in the CI aquifer and showing oxidising conditions (Eh ~+79 to +287 mV), and 4.5 ppm in the CT aquifer (A12) even though the recharge area to the NW (Atlas Mountains) is distant. All other CI samples were anoxic (DO below detection) and reducing (Eh −39 to −177 mV). There is therefore a downgradient redox zonation identified along the flow direction (Fig. 2). High DO (and NO_3) for the M'Zab waters confirms this region as a possible recharge direction, but these contents do not necessarily imply recent recharge and a modern water component; a ^{3}H level of 0.2 ± 1.0 TU (N.B. the TU represents one molecule of $^3H^1HO$ in 10^{18} molecules of (stable) ^1H_2O, with 1TU activity approximately equivalent to 0.118 Bq/kg – Stonestrom et al., 2013; this sample equivalent therefore to 0.02 ± 0.12 Bq/l) at Ghardaia (Guendouz, 1985) confirmed that water components at this site on the M'Zab Ridge have residence times > 30 a. Persistent DO has been observed also in deep waters up to 10 ka old, and up to 80 km from their point of recharge (Edmunds et al., 1982; Winograd and Robertson, 1982) possibly reflecting low levels of reducing agents such as organic carbon in the aquifer.

Uranium, Radium and Radon contents for both Algerian and Tunisian groundwater samples are given in Table 1, and whole-rock U/Th/K contents and U/Th activity ratios (A.R.s) in samples from core material for the (Tunisian) CI and CT aquifers in Table 2.

4.1. Uranium and ^{234}U/^{238}U activity ratios

Bulk sample ^{234}U/^{238}U and also ^{230}Th/^{238}U A.R.s for both the CI and CT cores samples (Table 2) are (within errors) ~1.0 confirming closed (rock) system conditions. Under closed system conditions, such as in rocks, ^{238}U-series radionuclides should come to secular radioequilibrium due to radioactive decay after 1.25 Ma such that their ^{234}U/^{238}U A.R. would be ~1.0 within the bulk of the rock matrix (Andrews, 1991). Surficial (open system), lacustrine/palaeolake carbonate deposits show significant deviation from unity (Fontes et al., 1992; Causse et al., 2003); however, Causse et al. (2003) have shown clustering of ^{234}U/^{238}U values discriminating Chott Djerid and Chott Fedjej deposits in Tunisia which might reflect differing groundwater discharge components from the CI or CT aquifers.

The downgradient evolution of dissolved U and ^{234}U/^{238}U in the Algerian CI groundwaters is shown in Fig. 2. Oxidising waters show dissolved U-contents of a few ppb (μg/kg). There is also an apparent decrease in ^{234}U/^{238}U A.R. with distance and increasing dissolved U-content to the identified redox barrier. After the redox barrier, the reducing waters (excepting El-Hadjira, A6) exhibit U-contents < 0.5 ppb, but an A.R. increase then in the reducing waters along the flow direction. Clearly the dominant factor controlling U in solution is the redox character of the waters.

All Algerian samples showed pH within the range 6.79–7.63, with values averaging 7.2 for the oxidising waters but trending in the reducing waters towards the lowest sampled pH value occurring at Gassi Touil (cf. Elliot, 1990). Uranium speciation modelling (Elliot, 1990) confirms the hexavalent (U6+) uranyl carbonate complex $UO_2(CO_3)_2^{2-}$ as the dominant dissolved species in the oxidising waters; aqueous carbonate complexation enhancing the mobility of the uranyl ion. Under very reducing conditions low levels of the tetravalent (U^{4+}) uranous–hydroxy complex $U(OH)_5^-$ become the dominant dissolved U species e.g. Rhourde El Baguel and Gassi Touil. All samples are undersaturated with respect to amorphous uraninite, UO_2(a) (mineral Saturation Index, SI: <−10 to −5); apparent mineral saturation is achieved with crystalline uraninite UO_2(c) for EI-Hadjira, Rhourde El Baguel, and Gassi Touil (SI: −0.07 to +1.85); and supersaturation with respect to coffinite ($USiO_4$) for the reducing waters (SI: +0.12 to +2.88). The Algerian CI waters contain dissolved silica levels ranging from 17 to 38 ppm, and in the reducing waters are saturated with respect to silica (both quartz and chalcedony). U-contents in the reducing waters are similar to the theoretical solubility limits for uraninite/coffinite ($\sum$U(IV) ~ 0.01 ppb) and for uranous hydroxy complexes with respect UO_2(c) (~0.05 ppb) for natural waters (Langmuir, 1978); a

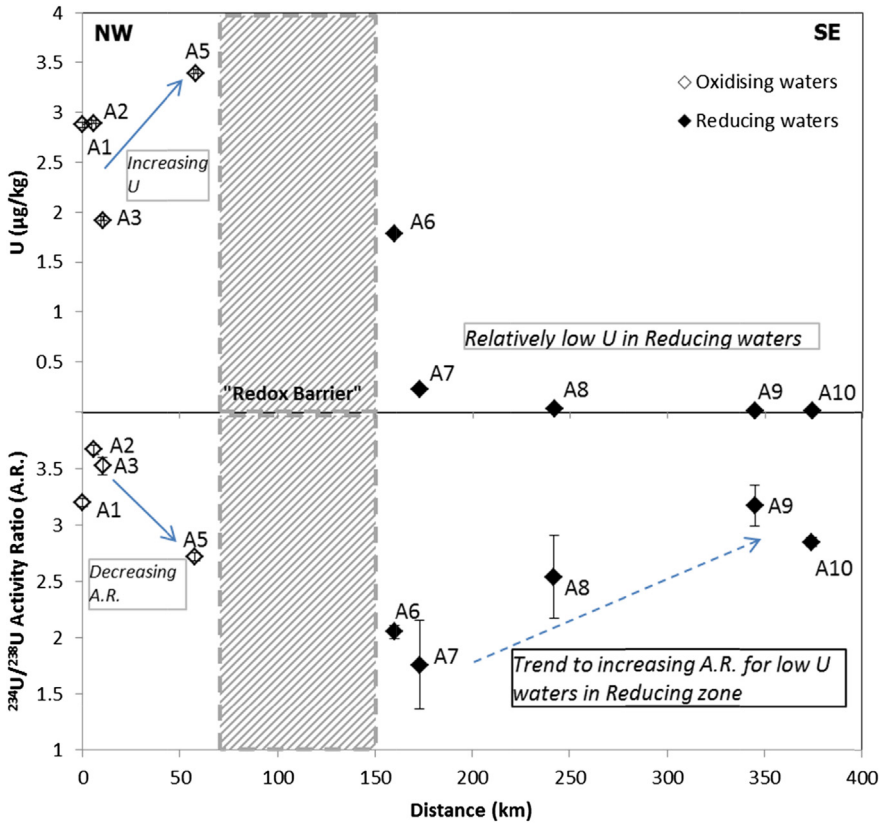

Fig. 2. U and $^{234}U/^{238}U$ A.R. evolution downgradient along the NW–SE flow line of the Algerian CI aquifer (A samples only). Open diamonds are oxidising waters, filled diamonds are reducing waters according to field Eh (redox) measurements. A redox boundary (hatched area) is defined between samples A5 and A6 based on field Eh values. Major trends are also shown (*see text*). Error bars are 2σ based on Poisson counting statistics.

Table 1
Radioelement contents and activity ratios of Continental Intercalaire (CI) and Complexe Terminal (CT) groundwater samples from Algeria and Tunisia.

Site number	Location	Aquifer formation	U (µg/g)	± SD	$^{234}U/^{238}U$ A.R.	± SD	^{226}Ra (mBq/kg)	± SD	$^{228}Ra/^{226}Ra$ A.R.	± SD	^{222}Rn (mBq/kg)	± SD
Algeria (A samples)												
1	Berriane 2	CI	2.874	0.014	3.19	0.02	16.28	1.11	0.65	0.10	14,171	222
2	Ghardaia	CI	2.894	0.014	3.67	0.02	24.42	2.59	0.80	0.12	8325	185
3	Metlili	CI	1.917	0.018	3.52	0.04	18.13	0.74	0.74	0.22	3626	111
4	Zelfana 1	CI					35.52	4.07			3663	111
5	Zelfana 4	CI	3.396	0.019	2.71	0.02	31.82	4.81	0.65	0.05	6179	148
6	El-Hadjira	CI	1.780	0.014	2.05	0.03	93.98	7.40	0.67	0.05	10,434	259
7	Ouargla 2	CI	0.222	0.003	1.76	0.20	54.02	4.44	1.04	0.12	31,487	37
8	Hassi Messaoud	CI	0.034	0.001	2.54	0.19	78.81	7.40	0.65	0.03	21,238	185
9	Rhourde El Baguel	CI	0.010	0.001	3.17	0.09	81.77	0.74	1.35	0.18	9028	111
10	Gassi Touil	CI	0.011	0.001	2.85	0.02	98.05	1.85	0.79	0.10	15,910	148
11	Djmaa 2	CI	0.031	0.001	4.06	0.23	92.50	5.55	0.42	0.08		
12	Djmaa 514	CT	5.498	0.041	2.70	0.02	39.59	1.11	1.01	0.13		
13	Chegga	CT										
14	Tolga	CI	0.042	0.001	2.46	0.09	101.75	4.81	1.32	0.14	11,507	259
Tunisia (T samples)												
1	Ksar Ghillane	CI	0.315	0.002	2.83	0.02	149.85	3.70	0.71	0.03	13,912	185
2	Oum el Farethe	CI	0.017	0.001	2.70	0.25	71.04	4.81	1.49	0.12		
3	Bou Abdellah	CI	0.045	0.002	0.40	0.03	105.08	5.18	1.16	0.07	8399	111
4	Menchia	CI	0.077	0.002	1.03	0.05	169.09	5.55	0.91	0.04		
5	Seftimii 3	CI	0.084	0.000	4.18	0.13	109.15	3.70	1.11	0.05		
6	Chott Fedjej 8	CI	0.036	0.001	1.06	0.05	566.84	9.99	1.05	0.02		
7	Chott Fedjej F2	CI	0.015	0.001	1.24	0.10	373.33	8.51	1.39	0.04	6105	37
8	Nefta	CI/CT	0.036	0.001	0.82	0.06						
9	Tozeur	CI/CT	0.025	0.001	0.52	0.04						
10	Mahassen	CI/CT	0.012	0.000	0.82	0.09						
11	El Mahadeth	CT	1.717	0.007	1.99	0.01	23.68	5.18	0.73	0.20	6216	37
12	Taouargha	CT	4.776	0.040	1.69	0.02	24.05	3.70	0.18	0.15		

N.B. All standard deviations (SD) are 1σ counting errors.
^{238}U activity may be calculated by ^{238}U (dpm/kg) = 0.7336*U (ppm); thence ^{234}U activity may be calculated from the A.R.
Similarly, ^{228}Ra activity may be calculated by multiplying ^{226}Ra by the A.R.

Table 2
U, Th contents and activity ratios (α-spectrometry) and U, Th, K contents (γ-spectrometry) of core samples of the Continental Intercalaire and Complexe Terminal of Tunisia.

α-Spectrometry

	Depth (m)	Sedimentary facies	U (μg/g)	±1SE	N	Th (μg/g)	±1SE	N	$^{234}U/^{238}U$ A.R.	±1SE	N	$^{230}Th/^{238}U$ A.R.	±1SE	N
Borehole F1 (Chott Fedjej, Continental Intercalaire)														
F1-1	753–759	Coarse sand with ≤25% shale	1.16	0.03	8	3.3	0.23	3	1.01	0.03	8	1.09	0.31	3
F1-2	795–799	Coarse/very coarse sand with quartz	1	0.07	2	nd			1.01	0.02	2	nd		
F1-3	813–823	Fine poorly cemented sandstone	0.93	0.03	3	nd			1.04	0.01	3	nd		
Borehole N6 (Negga, Complexe Terminal)														
N6-1	156–208	Limestone + some marl	2.65	0.05	2	1	0.1	2	1.04	0.02	2	0.95	0.07	2
N6-2	0–114	Argillaceous marl												
N6-3	116–155	Clays												

γ-Spectrometry

	Depth (m)	Sedimentary facies	U (μg/g)	±1SE	N	Th (μg/g)	±1SE	N	K (%)	±1SE	N
Borehole F1 (Chott Fedjej, Continental Intercalaire)											
F1-1	753–759	Coarse sand with ≤25% shale	0.74	0.07	4	4.4	0.67	4	1.005	0.006	4
F1-2	795–799	Coarse/very coarse sand with quartz	0.69	0.05	4	2.96	0.81	4	0.303	0.008	4
F1-3	813–823	Fine poorly cemented sandstone	0.62	0.15	4	2.37	0.98	4	0.568	0.006	4
F1-4	851–861	~50:50 sandstone + shale	1.08	0.12	3	6.79	1.39	3	1.673	0.009	3
Borehole N6 (Negga, Complexe Terminal)											
N6-1	156–208	Limestone + some marl	2.46	0.05	3	1.91	0.92	3	0.24	0.01	3
N6-2	0–114	Argillaceous marl	2.34	0.1	4	7.72	0.59	4	1.25	0.01	4
N6-3	116–155	Clays	1.15	0.13	4	5.28	0.72	4	0.88	0.01	4

N.B. Errors are 1 standard error (SE = SD/$\sqrt{N}$) based on *N* determinations.

level of only 8 ppb dissolved silica may be needed for mineral stability between $USiO_4$ and $UO_2(c)$, but a threshold of 60 ppm silica has been suggested on the basis of the common occurrence of co-existing quartz and uraninite mineral phases. Unfortunately, geochemical data are not available on the U-mineralogy of the CI aquifer formation to confirm the presence of either $UO_2(c)$ or $USiO_4(c)$ as the controlling mineral phases for U(IV)-deposition in the reducing waters.

In terms of $^{234}U/^{238}U$ evolution, on a standard plot (Fig. 3; Cowart and Osmond, 1980, their Fig. 4) oxidising waters (samples A1–A5) plot in Zone III (Forming accumulation) with a trend towards decreasing $^{234}U/^{238}U$ A.R. with increasing U-content down-gradient. Sample A6, identified from redox measurements as a reducing water, plots (Zone III) at its boundary suggesting active deposition. The reducing waters generally and characteristically plot in Zone IV (Normal Reduced), with increasing A.R. (samples A7–A10) for decreasing U-content. These trends are confirmed in a plot of $^{234}U/^{238}U$ versus 1/U (Fig. 4). Tunisian CI waters are also shown on Fig. 3, with samples T4, T6, T7 and also T2 plotting in Zone IV (Normal Reduced) and the first three samples suggesting a trend similarly to increasing A.R. for decreasing U-content as for the Algerian reducing waters (although their A.R. values do in fact lie within error of each). On a $^{234}U/^{238}U$ versus ^{234}U content plot (Fig. 5) the Algerian reducing water samples (A7–A10) follow an exponential trend of increasing A.R. with decreasing ^{234}U-content characteristic of deposition of U with α-recoil of ^{234}U from the surface of the solids into solution (or rather due to the α-recoil of its short-lived precursor ^{234}Th; cf. Andrews, 1991, his Fig. 15.4). The oxidising waters trend (cf. Fig. 2) suggests initially enhanced $^{234}U/^{238}U$ in the M'Zab waters then reflecting progressive U dissolution of the solids matrix back towards a bulk rock measured value of unity (Table 2). The initially enhanced values of $^{234}U/^{238}U$ here typically reflect the preferential dissolution of ^{234}U from the solids matrix due to radiation damage of the solids matrix during the decay process and/or α-recoil of the sort-lived ^{234}Th parent (Kigoshi, 1971; Andrews and Wood, 1972). In the reducing zone, as

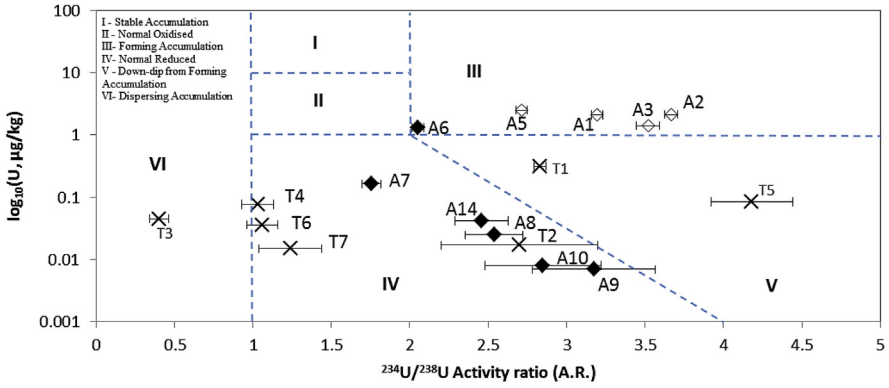

Fig. 3. Standard $\log_{10}(U)$ versus $^{234}U/^{238}U$ A.R. genetic plot (Cowart and Osmond, 1980) for both the Algerian (A) and Tunisian (T) CI aquifer waters. For the Algerian samples open diamonds are oxidising waters, filled diamonds are reducing waters according to field Eh (redox) measurements. The six genetic classification fields are identified as I–VI. Note particularly the linear trends apparent for samples A7–A10 (and including also A14) and T4, T6, T7 of increasing $^{234}U/^{238}U$ A.R. with decreasing U-content for Normal Reduced waters. Error bars are 2σ.

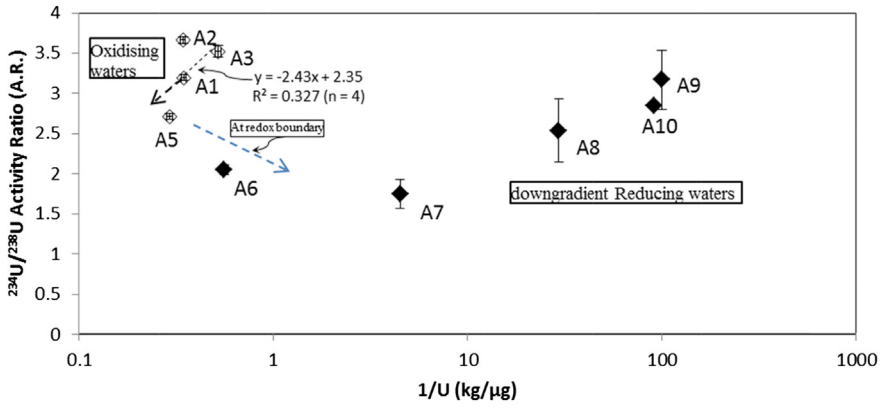

Fig. 4. $^{234}U/^{238}U$ A.R. plotted against 1/U and for the downgradient samples following the NW–SE flow line in the Algerian CI aquifer. Open diamonds are oxidising waters, filled diamonds are reducing waters according to field Eh (redox) measurements. Error bars are 2σ.

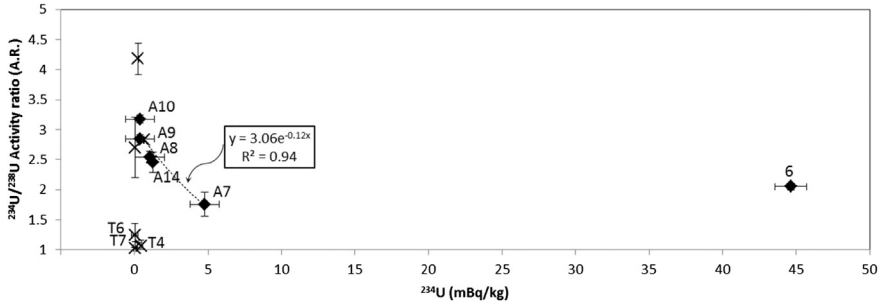

Fig. 5. $^{234}U/^{238}U$ A.R. versus ^{234}U for the Normal Reduced waters of the Algerian (A) and Tunisian (T) CI aquifer waters. Note the exponential trend fit of increasing AR above A.R. = 1 on the *y*-axis axis with decreasing ^{234}U content for the samples A7–A10 (and including A14) and also T4, T6, T7 and which follow deposition of U with α-recoil solution of ^{234}U (cf. Andrews, 1991, his Fig. 15.4, trend 1b). Error bars are 2σ.

chemical solution ceases and U precipitates to the solids surface the α-recoil process can dominate (cf. Kronfeld, 1974) enhancing the $^{234}U/^{238}U$ A.R. with increasing residence time (cf. samples A7–A10 downgradient, Figs. 2 and 4). Further downgradient of any active reducing zone (zone of precipitation) the injected ^{234}U sourced from the U precipitate becomes unsupported and decays.

For the Tunisian CI waters, only one ^{3}H measurement relevant to the sampled sites (Ksar Ghilane, 4 ± 3 TU; equivalent to around 0.5 ± 0.0.4 Bq/l, Stonestrom et al., 2013) is reported and cited radiocarbon activities again are generally low suggesting geochemical residence times again >20 ka (Annexe 8, OSS, 2003). Petersen et al. (2013) have suggested that in the Tunisian CI aquifer for U-contents <1 ppb the apparent trend is towards a decreasing $^{234}U/^{238}U$ A.R. following decreasing U contents and invoke an exponential decay relation (see Eq. (1b), Table 3) to explain this general trend and age date these waters. However, for the given samples here, Fig. 3 would suggest U-contents apparently decreasing in a S–N direction from Menchia (T4) to Chott Fedjej (T6, T7) with increasing $^{234}U/^{238}U$ A.R. similar to the model applied to the Algerian CI reducing waters. This would suggest a redox barrier occurring along this S–N direction. A similar S–N trend in the $^{234}U/^{238}U$ A.R.s can be seen in the data presented by Chkir et al. (2009) for samples East of the horst structure, and Petersen et al. (2013) also show samples showing a $^{234}U/^{238}U$ A.R. increase for decreasing dissolved U-content.

4.2. Radium and radon

Dissolved radium activities lie in the range 16–102 mBq/l for ^{226}Ra, higher than for bottled mineral waters but lower than the range seen for the Chott El Hodna groundwaters; a similar range is calculated for dissolved ^{228}Ra (11–134 mBq/l) in the deep Algerian CI waters. The two Algerian CT waters show similar activity levels to these CI waters. The Tunisian CI waters show enhanced Ra activities (71–567 mBq/l measured for ^{226}Ra; 106–595 mBq/l estimated for ^{228}Ra). The two Tunisian CT waters show just ~20 mBq/l.

In the oxidising Algerian CI waters their mean ^{226}Ra activity is similar to their mean ^{238}U activity, indicating chemical dissolution and weathering and in line with the trend to decreasing $^{238}U/^{234}U$ A.R. (Fig. 2). In the reducing waters, high measured dissolved ^{226}Ra contents occur with low U contents (similarly for the association of dissolved ^{228}Ra and U), simply reflecting the redox control on the solubility of the latter (Figs. 2 and 6). Nevertheless, the dissolved $^{228}Ra/^{226}Ra$ A.R.s within error generally cluster around the Th/U activity ratio of the aquifer core material (Fig. 7). Radium speciates predominantly as Ra^{2+} in groundwaters (Langmuir and Riese, 1985), and as a divalent alkaline-earth element the residence time of ^{226}Ra in solution is likely also controlled by congruent/incongruent solution of Ba and Ca as well as its half-life ($\tau_{1/2}$ = 1620 a). The downgradient trend in the Algerian CI waters is to increasing dissolved Ra following also enhanced contents in both Ca and Ba (Elliot, 1990). Ca- and Ba-contents generally are higher also in the Tunisian CI waters than the Algerian CI waters (Edmunds et al., 2003).

Dissolved ^{222}Rn activities lie in the range 3–32 Bq/l for the Algerian CI waters, higher than Algerian mineral waters but of a similar range to Chott El Hodna samples. The Tunisian CI waters show a similar range (6–14 Bq/l), with the single CT sample giving an activity at the lower end of this range. The ^{222}Rn activities in the Algerian and Tunisian CI waters generally are ~2–3 orders of

magnitude greater than precursor dissolved ^{226}Ra activities (Figs. 6 and 7). For ^{222}Rn, its solution in intergranular pore fluids is predominantly controlled by α-recoil from the rock surface and diffusional processes (Andrews and Wood, 1972). With a short half-life ($\tau_{1/2}$ = 3.825 d) equilibration is achieved in a groundwater residence time of just 25 d. The dissolved ^{222}Rn content, [Rn], in radioequilibrium with uranium in the solids matrix can be simply modelled as:

$$[\mathrm{Rn}],\ \mathrm{Bq}\Big/\mathrm{l} = 12.3 \times \Lambda_{\mathrm{Rn}} \times \rho \times \left(\frac{[\mathrm{U}]_{\mathrm{r}}}{\phi}\right) \quad (2)$$

where, 12.3 is the conversion factor for the specific degradation rate for ^{238}U, Λ_{Rn} is the fractional release efficiency for radon from the rock matrix, ρ is the rock density (g/cm^3), $[\mathrm{U}]_{\mathrm{r}}$ the U contents of the rock surface (μg/g) and ϕ is the fractional rock matrix porosity. Petersen et al. (in press) have highlighted that porosity measurements for the Continental Intercalaire are scarce, but suggest values between 22 and 26% in Algeria and 18% and 21% in Tunisia. For reasonable values then for a sandstone and for a coverage factor k = 1 (Elliot, 1990: Λ_{Rn} = 0.11 ± 0.01; ρ = 2.2 ± 0.3 g/cm^3; $[\mathrm{U}]_{\mathrm{r}} = 1 \pm 0.1$ μg/g (Chott Fedjej, Table 2); $\phi = 0.2 \pm 0.02$) then using Eq. (2) the calculated [Rn] = 15 ± 3 (1σ) Bq/l, generally in good agreement with observed activities in many of the CI waters (Fig. 7). Higher contents could reflect higher U contents or lower porosity. However, particularly the apparent "spike" in ^{222}Rn value at sample A7 (Fig. 6) considered alongside the downgradient profile for U (Fig. 2) might identify the position of a stable (Type 1) reducing barrier (Vogel et al., 1999, their Fig. 10); a stable barrier being one that has been established a long time compared to the half-life of ^{230}Th ($\tau_{1/2}$ = 75.2 ka; the precusor to ^{226}Ra). Potentially calculation of the recoil supply rate of ^{222}Rn to groundwater also can be used to assess the recoil supply of other nuclides to the aquifer, which for short-lived radionuclides then can be used to assess sorption characteristics (sorption rate constants and retardation factors) for the aquifer (Krishnaswami et al., 1982). The ^{222}Rn activities in the Algerian CI waters generally are ~2–3 orders of magnitude greater than precursor dissolved ^{226}Ra activities and similarly (up to two orders of magnitude) in the Tunisian CI waters, confirming that ^{226}Ra generally is not controlled simply by α-recoil, but likely by exchange at the rock surface.

Table 3
Calculated ^{234}U/^{238}U activity ratios (AR_t) for ^{234}U ingrowth following ^{234}Th recoil into pore fluids in the reducing zone of the Algerian CI sandstone aquifer after the model of Andrews et al. (1982).

Pore fluid residence time, t (years)	^{234}U/^{238}U activity ratio $(A.R.)_t$
1000	1.76
5000	1.78
10,000	1.80
20,000	1.85
50,000	1.97
75,000	2.07
100,000	2.16
250,000	2.59
500,000	3.01
750,000	3.22
1,000,000	3.32
1,250,000	3.37
1,750,000	3.41
∞	3.42

where,

$$AR_t = 1 + (AR_i - 1) \times e^{(-234\lambda t)} + 0.25 \times \rho \times S \times R \times \left(1 - e^{(-234\lambda t)}\right) \times \frac{[\mathrm{U}]_{\mathrm{r}}}{[\mathrm{U}]_{\mathrm{s}}} \quad (1a)$$

for,

AR_i, initial activity ratio as groundwater enters the reducing zone (i.e. $t = 0$) = 1.76 (Ouargla); $^{234}\lambda$, decay constant of ^{234}U = 2.795·10^{-6} a^{-1}; ρ, rock density = 2.2 g/cm^3 (typical sandstone); S, the extent of rock surface in contact with unit volume of groundwater = 100 cm^{-1} (Andrews and Kay, 1983); R, recoil range of ^{234}Th in the rock matrix = 3·10^{-6} cm (Andrews and Kay, 1978); $[\mathrm{U}]_{\mathrm{r}}$, U contents of the rock surface = 1 μg/g (Chott Fedjej); $[\mathrm{U}]_{\mathrm{s}}$, U contents of the solution = 6.4·10^{-5} μg/cm^3 (average of all the Normal Reducing waters).

Where the enhanced ^{234}U contents become unsupported then the right-hand term disappears (effectively, at the rock surface $[\mathrm{U}]_{\mathrm{r}} \rightarrow 0$) and a "decaying regime" occurs such that age of waters progressively downgradient can be dated as

$$t = \left(\frac{1}{234\lambda}\right) \times \left\{\ln\left[\frac{A_0 - 1}{A - 1}\right]\right\} = \left(\frac{\tau_{1/2}}{\ln 2}\right) \times \left\{\ln\left[\frac{A_0 - 1}{A - 1}\right]\right\} \quad (1b)$$

where A_0 is the A.R. upflow of the redox front (time $t = 0$ for the "decaying regime") and A the downgradient A.R. sample (Osmond and Cowart, 2000). Thus the excess ^{234}U injected into the water then decays. This is thought to happen where injected ^{234}U is substantially reduced in deeper zones (i.e. effectively a decrease in leach rates because of progressive depletion of ^{234}U in mineral surfaces downgradient) with U deposition and consequent (unsupported) excess ^{234}U decay.

4.3. Groundwater dating

For recoil-dominated environments ^{228}Ra/^{226}Ra A.R.s potentially can be up to the order of twice that of the parent radionuclides in 'old' groundwaters, such that higher ^{228}Ra/^{226}Ra A.R.s might be an indicator of groundwater maturation (Davidson and Dickson, 1986). The closeness of measured ^{228}Ra/^{226}Ra A.R.s to the rock Th/U production ratio suggests that the α-recoil coefficients for the parent nuclides are about equal, and that Th adsorption from weathering is minimal (Porcelli, 2008). ^{222}Rn/^{226}Ra A.R.s presuming a rock surface in which ^{230}Th, ^{226}Ra and ^{222}Rn are in radioequilibrium suggest groundwater residence times of only 2–20 a (Andrews, 1983; Elliot, 1990), but this estimate likely reflects other controls on ^{226}Ra than simply an α-recoil mechanism, as discussed previously.

Once a groundwater has become so reducing in character that chemical leaching of ^{234}U ceases then the ^{234}U/^{238}U A.R. may evolve in time as a balance between ^{234}U leaching (α-recoil) and its decay (Eq. (1a), Table 3). Table 3 shows estimated A.R. evolution with time (t) for the Algerian CI samples A7–A10 based on the trend seen in Figs. 3 and 5 and using Ouargla (A7) as starting ^{234}U/^{238}U value influent to this zone (given this is the initial low U sample encountered downgradient). Given infinite time, the dissolved ^{234}U/^{238}U of waters could evolve to a maximum value ~3.4 under these conditions. An increase of A.R. from 1.76 to 3.17 potentially could take 500–750 ka (the generated A.R.s for these residence times bracketing the sample value seen at Rhourde El Baguel (A9); Table 3). For the flow distance Hassi Messaoud – Rhourde El Baguel/Gassi Touil the groundwater residence time ~65 ka. These (geochemical) age estimates are relative residence times starting from the location sample A7 to that of sample A10 on top of the absolute age of the water at location sample A7. Nevertheless, such residence times clearly suggest a palaeoage status for the waters downgradient of Ouargla (A7).

For the Tunisian waters, using Menchia (T4) as the AR_i = 1.03 and mean U content for the Normal Reducing waters (Figs. 3 and 5), would suggest a potential maximum A.R. generated ~5.3 (Eq. (1a), Table 3), and a residence time ~20 ka then from the observed A.R. of 1.24 at Chott Fedjej (T7).

Further support for the characterisation of the water samples as being old, palaeowaters is provided both by dissolved ^{4}He-contents and recharge temperature (RT) estimates based on other dissolved noble gases (Ne, Ar, Kr, Xe; Andrews and Lee, 1979; Elliot, 1990). Along the given flow direction in the Algerian CI, ^{4}He-contents cumulatively increase (Fig. 8). Even without a detailed model for He-release (cf. Castro et al., 2000) this downgradient ^{4}He trend

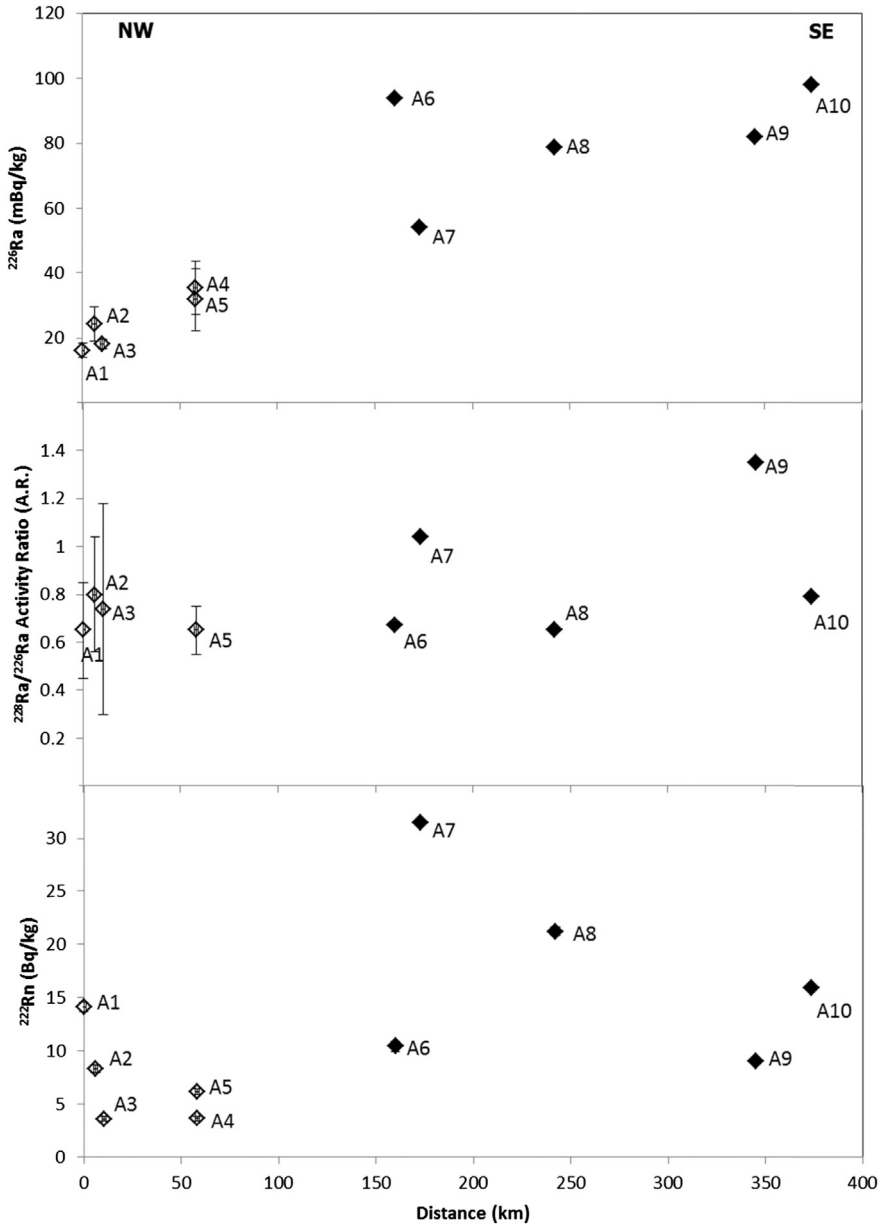

Fig. 6. Measured ^{226}Ra, ^{228}Ra/^{226}Ra A.R. and ^{222}Rn evolution downgradient along the NW–SE flow line of the Algerian CI aquifer. Open diamonds are oxidising waters, filled diamonds are reducing waters according to field Eh (redox) measurements. Error bars are 2σ.

supports the idea of progressively more mature waters along this flow direction. A groundwater "age" can be calculated based simply on the production terms for the radioactive decay of U, Th and their radioactive α-emitting daughters in the rock matrix:

$$t(a) = \frac{([\mathrm{He}] \times \phi)}{(\rho \times G)} \quad (3)$$

where [He] is the dissolved 'excess' (radioactive) groundwater ^{4}He-content in cm^3 STP cm^{-3} H_2O (ie cc STP gas per cc water, after accounting for atmospheric air components), and $G = \{1.19 \times 10^{-13}\ [\mathrm{U}]_r + 2.88 \times 10^{-14}\ [\mathrm{Th}]_r\}$ is the He-generating rate function and where $[\mathrm{Th}]_r$ now is the thorium content (ppm) of the rock matrix; all other symbols and adopted values have been defined previously (Eqs. (1a) and (1b); Table 3). Estimated residence times are 13–76 ka for the M'Zab waters (in line with ^{36}Cl age estimates by Guendouz and Michelot, 2006), 45 ka at Tolga and up to 1.75 Ma at Gassi Touil. The age difference estimated downgradient specifically between Hassi Messaoud and Rhourde El Baguel/Gassi Touil by ^{4}He is an order of magnitude higher than for ^{234}U/^{238}U modelling, although similar to the estimate of potentially ~500 ka generally to achieve the most enhanced A.R. for waters in the reducing zone, and supporting this latter estimate. This simple model (Eq. (3)) assumes all the ^{4}He generated is dissolved in the porosity, and as such these are conservative, minimum estimates of ages. An alternative formulation using ^{4}He/^{222}Rn ratios (Torgersen, 1980) would suggest residence times up to an order of magnitude greater for the youngest waters than those calculated simply by Eq. (3) (Elliot, 1990). Elliot (1990) has also modelled ages based on crustal diffusive loss model (Andrews, 1985) which suggests that the generating function potentially could be just 1–2% of the cumulative ^{4}He produced over the age of the Continental Intercalaire formation. Thus, although generally giving enhanced age estimates in absolute terms, these relative ^{4}He ages nevertheless clearly suggest

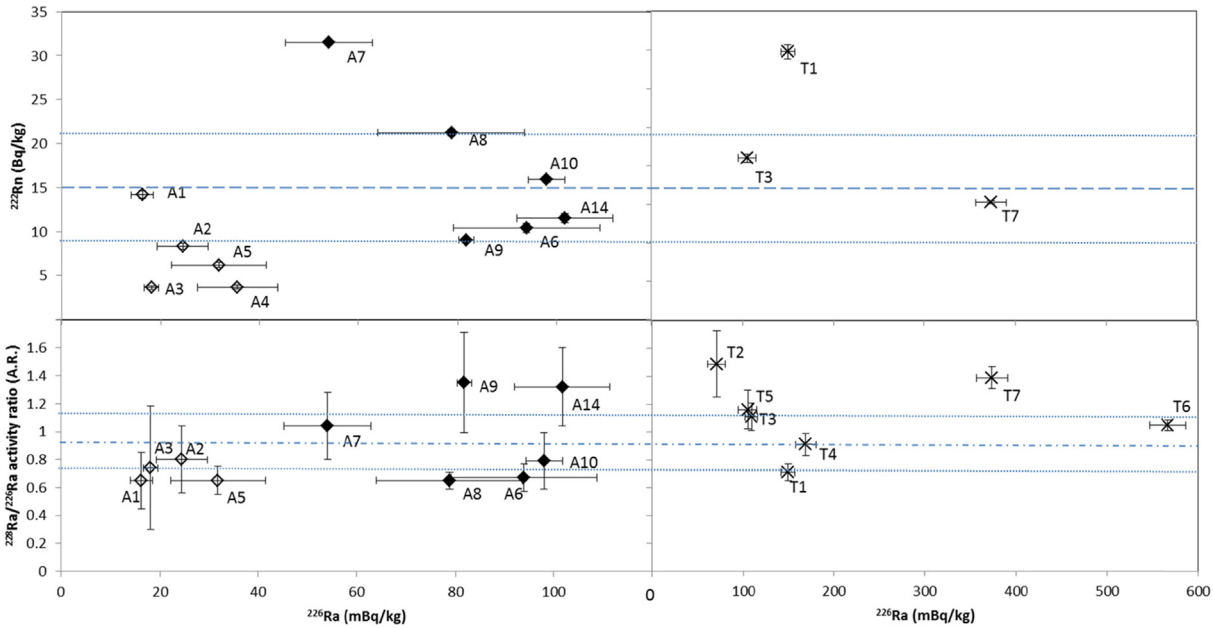

Fig. 7. Measured $^{228}Ra/^{226}Ra$ A.R. and ^{222}Rn plotted against ^{226}Ra for both Algerian (*left*) and Tunisian (*right*) CI waters. For the Algerian waters, open diamonds are oxidising waters, filled diamonds are reducing waters according to field Eh (redox) measurements. Error bars are 2σ. Also shown (broken lines) are: (top) the estimated content of ^{222}Rn in equilibrium with the rock matrix (Eqs. (1a) and (1b)) and 2σ error bands (see text); (bottom) the average $^{232}Th/^{238}U$ activities for the CI (Tunisia) core material (Table 2) with 2σ error bands.

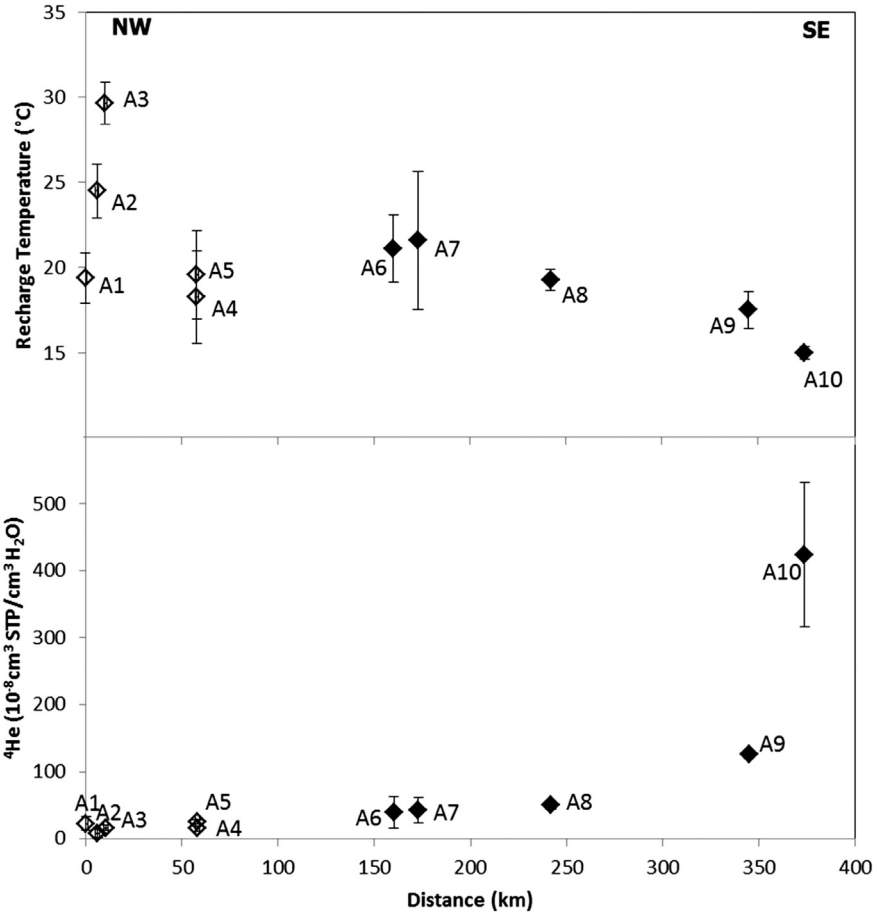

Fig. 8. Recharge temperature (RT) estimates (based on dissolved Ne, Ar, Kr, Xe gas contents) and (radiogenic) excess ^{4}He corrected for 'excess air' and air-equilibration (taking ^{4}He solubility ~4.6×10^{-8} cm^3 STP/cm^3 H_2O @20 °C) components along the NW–SE flow line of the Algerian CI aquifer. Error bars are 2SE.

increasing groundwater ages downgradient for the Algerian CI waters; a general linear trend of increasing ^{4}He with Cl^{-} is also evidenced for these waters (Elliot, 1990). Concomitantly, recharge temperatures (RTs) calculated from dissolved noble gas contents (Fig. 8) are ≥19 °C for the M'Zab Ridge (samples A1–A5) but appear to decrease significantly in the central basin (~15 °C at (A10) Gassi Touil).

The three Tunisian CI waters sampled for dissolved noble gases (T1, T3, T6) suggest ^{4}He ages from around 660 ka up to 1.3 Ma, and show RTs around 18–19 °C. Recent $^{3}He/^{4}He$ measurements in the Tunisian study area attest that high He contents here are crustal in origin but that the enhanced contents may be associated also with local complex geology (e.g. faulting) and tectonics (Fourré et al., 2011).

The estimated noble gas RTs generally are somewhat cooler than current WMO Climate Normals (CLINO) data with climatological standards for 1961–1990 (the latest global standard normals period) for dry bulb annual average temperatures being 21.8 °C (Biskra, Algeria), 21.7° (Tamanrasset, southern Algeria) and 19.5 °C (Gabès, Tunisia) (WMO, 2014). Thus RTs generally suggest cooler waters than present climatic conditions, and alongside the given age estimates affirm the palaeowater status of both Algerian samples (especially towards the centre of the Grand Erg Oriental basin) and some CI Tunisian waters.

For the Complexe Terminal samples, using $[U]_r = 2.65$ μg/g, $[Th]_r = 1$ μg/g (Table 2), the single Tunisian CT sample (El-Mahadeth) suggests a significant ^{4}He age of 25 ka alongside a noble gas RT of 23.4 °C. Data published by Guendouz et al. (1997) also show significant (radiogenic) 'excess' ^{4}He-contents for Algerian CT samples which suggest model ^{4}He ages (Eq. (3)) of the order 62 ka (Hassi Messaoud), 34 ka (Rhourde El Baguel) and 46–76 ka (Gassi Touil) alongside reported RTs ranging 18.3–21.4 °C.

5. Conclusions

Dissolved Rn contents in the deep Continental Intercalaire (CI) aquifer of Algeria and Tunisia show activities 3–32 Bq/l, slightly higher than activities shown in Algerian bottled mineral waters but similar to activities seen in other deep wells from sandstone aquifers in SE Algeria and also shallow groundwaters from around the Chott El Hodna to the North of the current study area. The Algerian and Tunisian CI activities for ^{222}Rn appear to be generally in secular radioequilibrium with a rock U-content of ~1 ppm (as measured in (Tunisian) CI core sample) and for a porosity ~20%%; however the enhanced value at Ouargla may identify the presence of a stable-type redox barrier in this locale. Radium contents (^{226}Ra, ^{228}Ra) are 10–135 mBq/l in the Algerian CI waters, and up to 600 mBq/l locally associated with Chott Fedjej in Tunisia. These activities are higher than for mineral bottled waters and reported groundwaters in Algeria. Activity ratios for $^{226}Ra/^{228}Ra$ generally cluster around the Th/U activity ratio for the CI core material as the predominant source. Activities are orders of magnitude less than for dissolved ^{222}Rn, showing that Ra contents are not recoil-dominated as they are for ^{222}Rn. The highest Ra activities appear positively correlated with Ca and Ba contents.

U-contents and $^{234}U/^{238}U$ activity ratios following a flow line NW–SE from the M'Zab Ridge in the Algerian CI identify a redox zone downgradient where A.R.s are enhanced as dissolved U-contents decrease to <1 ppb, and showing α-recoil of ^{234}U from the rock surface enhanced by U precipitate as the dominant source. Modelling of the residence times to generate the enhanced A.R.s, starting from a value of from 1.76 (at the start of the recoil-dominated zone) to maximum 3.17 downgradient, suggest residence times up to ~600 ka; the distance between Hassi Messaoud and Rhourde El Baguel (some 100 km) apparently taking ~65 ka. In Tunisia, a similar trend U-contents and $^{234}U/^{238}U$ activity ratios is suggested going S–N and implicating a recharge direction from the Tinrhert Plateau of SE Algeria or the Tunisian Dahar Hills towards the Chott Fedjej discharge zone, as indicated also by the aquifer piezometry. This trend indicates also a redox barrier occurring in this S–N direction. Age modelling of the $^{234}U/^{238}U$ evolution suggests geochemical residence times ~20 ka between Menchia and Chott El Fedjej in Tunisia.

The paleoage status of these Algerian and Tunisian waters is supported by simple modelling of ^{4}He accumulation (and $^{4}He/^{222}Rn$) in the waters which suggest water ages of the order tens of thousands up to 1 Ma old. The palaeowater status of these waters is supported also by recharge temperatures measured for the CI waters, which are generally cooler than current Climate Normal values for annual temperature in the region and in the case of Gassi Touil (RT ~ 15 °C) indicate recharge under significantly cooler (past) climate conditions.

The $^{234}U/^{234}U$ activity ratios seen in waters from both the Algerian and Tunisian aquifers therefore support previous ^{14}C and ^{36}Cl age estimates that identify the Continental Intercalaire waters from the M'Zab ridge towards the centre of the Grand Erg Oriental sub-basin in Algeria as being palaeowaters, and similarly for waters in the locality of Chott Fedjej to the East of the major horst structure that occurs around Chott Djerid in Tunisia.

Finally, old water ages (residence times) are suggested also for the few Complexe Terminal (CT) waters presented from Algeria and Tunisia, since these samples again have enhanced (radiogenic) ^{4}He contents.

For the regions studied therefore these waters should be regarded as "*fossil*" waters and treated effectively as a non-renewable resource. Nevertheless, any such geochemical residence time estimates may require reconciliation with hydraulic and emerging geophysical approaches, especially on the margins as recognised by Gonçalvès et al. (2013). For example, for identified palaeowaters in the centre of the regional, fissured London Basin Chalk aquifer (UK) Elliot (1999) invokes matrix exchange effects on solute transport to reconcile apparent geochemical residence times with the much younger hydraulic transit time estimates.

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